

**Comment on “Negative Heat Capacity for a Cluster of 147 Sodium Atoms”
by Schmidt et al.**

In a recent letter [1], Schmidt et al. analyze a region where the specific heat of a Na_{147}^+ cluster becomes negative. In Boltzmann-Gibbs (BG) statistical mechanics the specific heat can never be negative in the canonical ensemble. However, as the authors are well aware, no such property is valid in general for the microcanonical ensemble. This is indeed the case of a variety of physical situations ranging from self-gravitating systems to melting atomic clusters and fragmenting nuclei (see [1] and references therein). An important feature that all such systems have in common is thermodynamic *nonextensivity*, reflected, as also mentioned in [1], in the fact that the energy associated with N particles is not proportional to N . Nonextensivity occurs everytime *the range of the interactions is not negligible compared to the (linear) size of the system*. Two important physical examples are:

- *short-range interactions in small systems*
- *long-range interactions* in systems of any size [2–4].

Now, if the system is isolated, nonextensive, in an equilibrium-like state, and exhibits, for some energy range, a negative specific heat, then not one but at least two possibilities must be considered:

1) the system is in its thermodynamically stable state and then the BG microcanonical ensemble is to be used, as preconised in [5] and done in [1].

2) the system is in some kind of dynamic *metastable state*, and then some other thermostatical approach might well be necessary. One such alternative description is nonextensive statistical mechanics [3], which has proved to be useful in a variety of complex situations (e.g., fully developed turbulence [6], electron-positron annihilation producing hadronic jets [7], motion of *Hydra viridissima* [8]).

The metaequilibrium state to which we make reference as a second possibility has indeed been observed in magnetic-like Hamiltonians such as arrays of long-range coupled planar rotators (the so called HMF [9] and its generalization, the $\alpha - XY$ model [10]), among

others, including fluid-like systems [11]. To illustrate this point, we report in fig. 1 a numerical simulation typical of the relaxation process in the HMF model. As a function of time, two plateaux are observed for the average kinetic energy per particle and the BG formalism is violated for the first plateau (panel a), where we find a region of negative specific heat (panel c) [18]. More precisely, the velocity distribution is well described by the standard Maxwellian in the late plateau (panel b), whereas for the early plateau it appears to be described by the type of distribution emerging within nonextensive statistical mechanics [18]. Similar results and anomalies have been recently described in other models, including first order phase transitions [12–14].

The relevance of long range interactions in sodium clusters and similar atomic liquids is well known [15]. Consequently metastable states could very well occur in relatively small clusters such as those studied in [1], as in various colloidal glasses [16] and other clusterized systems [17]. For example, in colloidal glasses it is common belief that the structural arrest at the glass transition is due to the increasingly size of strongly cooperating sets of atoms [16]. Under these circumstances, and without further experimental evidence, application of BG equilibrium statistical mechanics in [1] might have no support. Since the analysis of the authors only applies to one among at least two physically important possibilities, the theoretical interpretation they draw from their experiments [1] is not necessarily true.

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FIGURES

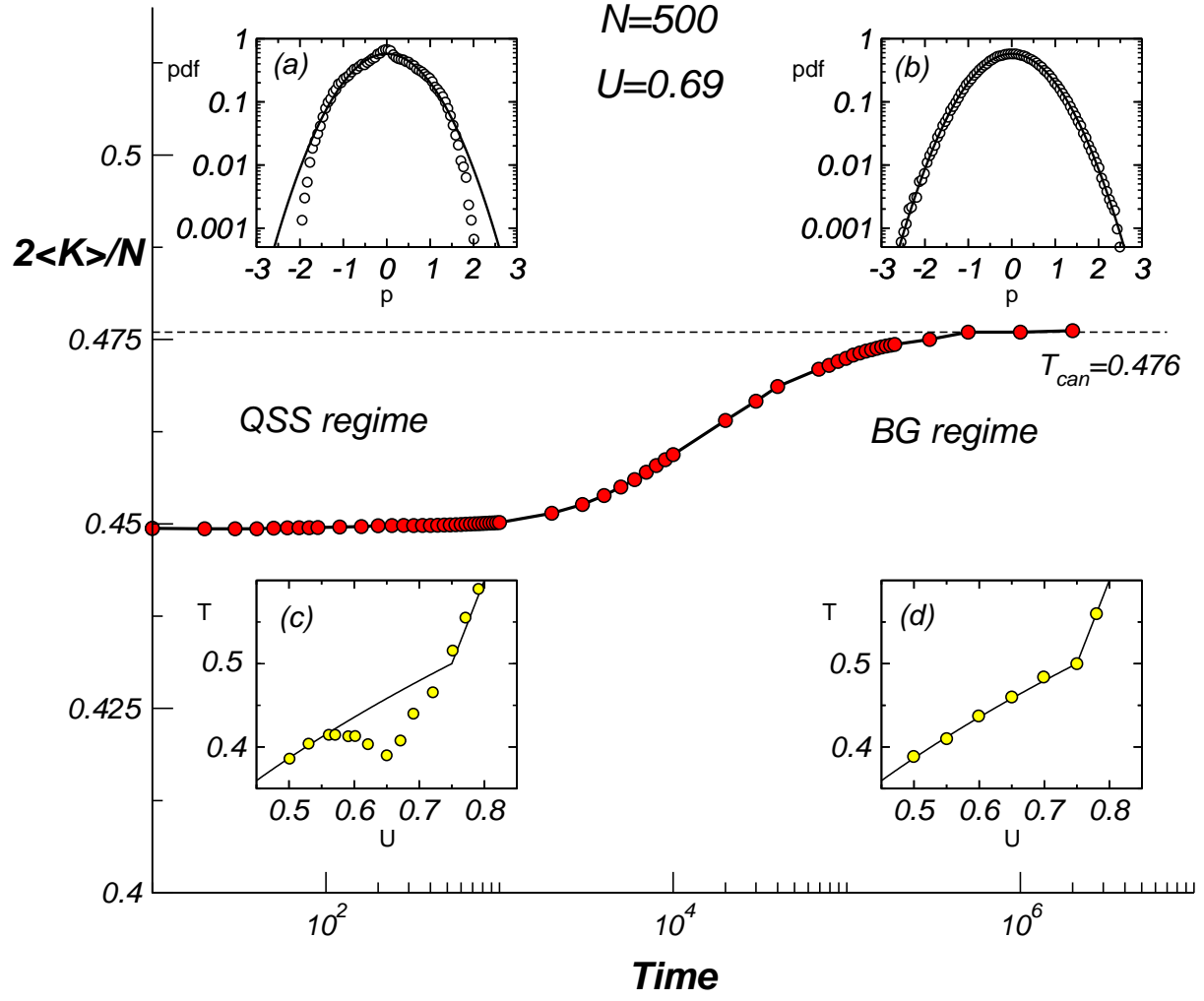


FIG. 1. Time evolution of twice the average kinetic energy per particle (“temperature”) for a HMF system with $N=500$ (red circles) at energy per particle $U = 0.69$. The corresponding velocity distribution is *not Maxwellian* for the first, metastable plateau (panel (a)), whereas standard statistical mechanics is valid for the second, stable plateau (panel (b)), open circles. The Gaussian canonical prediction is also shown as a full curve. Correspondingly, we find a negative specific heat, $C_V = dU/dT$, in the metastable state (Quasi-Stationary State (QSS) regime), as shown in panel (c) (open circles) in comparison with the canonical caloric curve, while the specific heat for this hamiltonian is always positive when BG equilibrium is reached (panel (d)). Such anomalies are strongly related to nonextensivity and have been found in various systems [11,12,14,18].